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ELECTRONIC PROCESSES IN EXPLOSIVES INITIATION

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Picatinny Arsenal
Dover, New Jersey

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Pseudostable materials undergo decomposition into a more stable form by rapid self-sustaining decomposition, deflagration, or detonation. The materials are pseudostable because the initiation of the reaction requires that some activation energy be supplied by an external stimulus. Traditionally the stimuli have been considered to be either thermal or mechanical in origin, and little consideration has

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20. Abstract (Continued)

been given to the role of electronic processes in initiation. This work describes the determination of the electronic energy level structure in explosives using low temperature optical absorption techniques and the determination of electronic transport properties by photoconductivity and related solid state measurements. Madelung potentials and electric energy levels were theoretically determined and indicate the nature of the bonding within the explosive crystal lattice. The possibility of the nonthermal, photo-electronic initiation effect was first predicted by our theoretical studies. These studies have focused on the relationship between the chemical pseudostability of explosives and their electronic structure and have suggested novel mechanisms for initiation of primary and secondary explosives, propellants, and pyrotechnics. Specifically, photo-electronic initiation has been observed in lead and thallous azide. The effect has been characterized and interpreted in terms of the optical and electronic transport measurements on these materials.

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INTRODUCTION

In the mid to late 19th century, major advances in explosives technology resulted both from the discovery of nitroglycerine and the invention of explosive trains. In an explosive train, the output from small quantities of sensitive primer or primary explosive is used to initiate successively less sensitive but more energetic and massive quantities of secondary explosives. In general practice, the sensitive primary explosive is kept physically separated from the secondary explosive until the last practical moment before initiation. However, the very property of primary explosives which makes them so important and useful in this context--their sensitiveness or ease of initiation--remains a serious hazard during manufacture and handling and a frequent cause of malfunction in munitions. Thus a further advance in explosives technology comparable to the 19th century discoveries would be the invention of schemes to initiate secondary explosives reliably and directly. Before such an advance can be made, however, much has to be learned about the initiation of detonation in materials.

Reported here are the preliminary results from a concerted theoretical and experimental effort to (a) gain an understanding of the initiation of primary and secondary explosives, (b) discover new mechanisms for the initiation of primary explosives, and (c) discover methods for the direct initiation of secondary explosives, possibly eliminating the need for primary explosives.

The approach is wide ranging, considering both inorganic and organic explosives. It includes advances in both theoretical and experimental solid state physics in general and the application of these advances to the study of complex explosive solids. Initially, the theoretical basis for the relationship between chemical instability and electronic structure will be reviewed. Next, the determination of the electronic energy level structure and the electronic transport of inorganic azides both experimentally and theoretically will be considered. Based on this information, the validity of the premise that electron transfer processes can lead to direct, non-thermal initiation of primary inorganic explosives will be determined. Finally, the extension, both theoretically and experimentally, of these techniques to the possibility of direct, non-thermal initiation of secondary explosives will be considered.

GENERAL THEORY

Explosives are members of a class of materials which can exist at normal temperature as pseudostable solids. They undergo decomposition into more stable compounds by rapid self-sustaining decomposition, deflagration, or detonation. They are pseudostable because initiation of the reaction requires that some activation energy be supplied by an external stimulus as illustrated in a reaction coordinate diagram (Figure 1). R is a generalized reaction coordinate describing the chemical state of a system and can represent, for example, the distance between atoms in a molecule or solid. The effective potential energy (V_{eff}) of an explosive or energetic solid in a pseudostable state is located at a local minimum corresponding to R_1 in Figure 1. If the system receives the activation energy E_a, chemical reaction takes the system to the state represented by R_2 with the release of chemical or explosive energy E_r.

Any given explosive has a number of reaction coordinates and reaction paths of the type shown in Figure 1. The quantity of energy required to initiate the explosive reaction, E_a, is different for each explosive and is in general different for each reaction path for a given explosive. This leads to differences in observed activation energies depending on the explosive material, the stimulus, and the effective localization of energy input. Materials with small activation energies may be easily initiated and are classified as sensitive or primary explosives. For some materials, the activation energy may be appreciable (secondary explosives), requiring the use of strong shock waves from sources such as primary explosives to supply the necessary energy for initiation.

It is almost universally [1] assumed that the stimulus supplying the activation energy is first converted into heat, no matter whether it was initially mechanical, electronic, or thermal in origin. The horizontal lines in Figure 1 represent excited vibrational states of the molecule or solid. Thermal initiation corresponds to raising the local temperature, increasing the excursions of the atomic vibrations, or populating higher excited vibrational states until the activation energy is supplied.

It has been postulated that initiation of reaction and of detonation could arise from purely photochemical processes or by direct excitation of the electrons within the explosive molecules or solid. [2] Demonstration of this speculation has been lacking due to the absence of a strong theoretical basis and the ambiguity of much of the experimental evidence.

More recently, Williams [3] has considered from a general theoretical point of view the relationship between the electronic energy states or the electronic structure and chemical instability or initiation.

According to quantum mechanics, all information about a physical system is contained in its wavefunction $\psi(\underline{r},\underline{R})$. The coordinate $\underline{r}$ stands for all the electronic coordinates while $\underline{R}$ represents the coordinates of the nuclei. This wavefunction satisfies the Schrödinger equation:

$$H\,\psi(\underline{r},\underline{R}) = E\,\psi(\underline{r},\underline{R}), \qquad \text{II-1}$$

where H is the Hamiltonian operator containing the kinetic energies of all the particles (nuclei and electrons) and all the potential interactions and E is the energy eigenvalue. From the difference in mass of the electrons m and the nuclei M_j and from equipartition of energy, it is evident that the electrons move much more rapidly than the nuclei. Thus at each instant, the motion of the electrons or the electron distribution can be determined as though the nuclear positions or coordinates were fixed. The electronic motion can then be determined parametrically as a function of the nuclear coordinates since the electrons exist in separable, approximate stationary states that are smoothly modified by the motion of the nuclei. This is the adiabatic approximation of Born and Oppenheimer.[4] In accordance with the adiabatic approximation, the wavefunction can be put into the following form:

$$\psi(\underline{r},\underline{R}) = \phi_{\underline{R}}(\underline{r})\ \chi(\underline{R}); \qquad \text{II-2}$$

$\chi(\underline{R})$ describes the state of the nuclei and $\phi_{\underline{R}}(\underline{r})$ the state of the electrons about fixed nuclear coordinates $\underline{R}$. The stationary electronic states are determined from the following Schrödinger equation where the nuclei are taken to be fixed:

$$H_{el}\ \phi_{\underline{R}}(\underline{r}) = E_{el}(\underline{R})\ \phi_{\underline{R}}(\underline{r}), \qquad \text{II-3}$$

where H_{el} is that part of the total Hamiltonian operator containing the electronic coordinates only, $E_{el}(\underline{R})$ are the electronic eigenvalues or electronic energy levels, and $\underline{R}$ specifies the fixed nuclear positions $\underline{R}_1 \ldots\ldots \underline{R}_n$. The equation describing the motion of the nuclei is approximately:

$$\{ - \sum_j \frac{h^2}{2M_j} \nabla^2_{\underline{R}_j} + V(\underline{R}) + E_{el}(\underline{R})\} \chi(\underline{R}) = E\chi(\underline{R}), \qquad \text{II-4}$$

where the first term represents the kinetic energies of the nuclei and $V(\underline{R})$ the potential interactions between nuclei. The validity of the approximations used in deriving this equation, particularly for large excursions in $\underline{R}$ occurring during chemical reactions, has been discussed in detail by Williams.[3]

Assuming the approximate validity of the preceding equation, it is clear that the motion of the nuclei is determined by the effective potential

$$V_{eff}(\underline{R}) = V(\underline{R}) + E_{el}(\underline{R}). \qquad \text{II-5}$$

Thus the important conclusion is that the motion of the nuclei depends not only on the internuclear interactions but depends, in addition, explicitly on the electronic state of the system, $E_{el}(\underline{R})$. A schematic presentation of this concept appears in the reaction coordinate diagram, Figure 2. The shape of V_{eff} can be quite different for the electronically excited state E'_{el} than for the electronic ground state E_{el} with a lower activation energy. For other electronically excited states such as that represented by E''_{el} in Figure 2, a substance when excited to this electronic state would be completely unstable since there is no activation energy required to lead to the lower decomposed state. Thus even at low temperatures, characterized by small atomic vibrations, it would be possible in this system to initiate decomposition purely by excitation to this excited electronic state.

Thus in general, states of electronic excitation in a chemical system can determine the manner in which chemical reaction proceeds. When the chemical system is an explosive, radically different modes of initiation of reaction from those used traditionally are possible. Specific initiation mechanisms will depend on the excited electronic states or on the fundamental electronic properties of particular explosive substances.

FUNDAMENTAL ELECTRONIC PROPERTIES

The electronic energy levels of a solid are arranged in a fashion similar to their arrangement in the free atoms or molecules which comprise the solid with several critically important differences. In the solid all of the electronic particles interact, perturbing the atomic or molecular electronic states so that they appear as energy bands rather than discrete levels of energy.[5] The bands of energy are separated by energy regions for which no electron energy states are allowed; such forbidden regions are called energy gaps or band gaps. The highest energy band filled with electrons is called the valence band and the next higher band (which is not completely filled) is called the conduction band. Electrons excited to the latter band may move under the influence of an electric field, giving rise to electronic conduction.

The widths of the energy bands, the band gap separation between them, and other features of the bands are referred to as the electronic band structure or the electronic energy level structure. Relatively small differences in the electronic energy level structure can lead to quite marked differences in the behavior or properties of solids. For example, the distinction between insulators, semiconductors, and metals can be made solely on the basis of energy band gap widths and on the distribution of electrons within the band structure. A detailed knowledge of the band structure and of the transport properties of electrons in such semiconductors as germanium and silicon has led to the development of new semiconducting materials and devices such as the transistor and to the discovery of new materials for fluorescent lighting and new optical systems such as solid state lasers. The critical question is whether a similar understanding of the electronic structure of explosive solids can be exploited for discovering equally new and important applications.

A. Experimental

The first step in addressing this question is to determine the energy level structure of selected explosive solids. This is a formidable task even for simple metals or semiconductors requiring the use of many highly sophisticated techniques. In order to obtain useful information on even the simplest explosive, it has been necessary to develop new techniques suitable for measuring small (safe) quantities of explosives and to prepare explosives with a degree of control never previously attained.

Because of its relative simplicity (compared to other explosive solids) and extensive utilization as a commercial and military primary explosive, lead azide was selected as the first explosive to be extensively investigated. The most powerful technique for the determination of the band structure is the measurement and analysis of the optical absorption of the solid. The absorption coefficient or fraction of light absorbed in passing through a sample (usually a thin crystal or thin film) is measured as a function of wavelength or energy and is described by

$$I = I_o e^{-\alpha d} = I_o 10^{-O.D.} \qquad \text{III-1}$$

where I_o and I are the intensities of the incident and transmitted light beam respectively, α is the absorption coefficient, d is the sample thickness, and O.D. is the optical density (the experimental parameter determined most directly). The most basic information about the band structure of the ideally pure material is obtained in the energy region corresponding to excitation of an electron from the valence band to the conduction band. The empty energy state in the valence band (absence of valence band electron) created by the excitation is called a hole. Some absorption of incident light occurs for photon energies just less than that necessary to excite electrons completely across the energy gap; it is characteristic of bound pairs of electrons and holes, called excitons. The energy region near the band-to-band transition (fundamental absorption) is characterized in most materials by absorption coefficients of the order of $\alpha = 10^5$ cm^{-1}. Spectrophotometers can measure optical densities of approximately 1-5, and thus from Equation III-1 the sample thickness is required to be about 10^{-5} cm. For most materials, samples of this thickness are usually in the form of thin films prepared by sublimation or evaporation from solutions. None of these techniques could be utilized with lead azide since it cannot be sublimed and is highly insoluble. A novel technique [6] was developed in which metallic lead films were evaporated onto appropriate substrates and subsequently reacted with gaseous hydrazoic acid (HN_3). Thin films of excellent optical quality were obtained, and the fundamental optical absorption of lead azide was measured [6] for the first time (Figure 3).

Because of the complexity of the azides, additional information was required before a realistic model of the electronic band structure could be deduced. Another extremely powerful technique was used which gives additional information about the band structure and also characterizes the electronic transport properties. When light of a wavelength corresponding to the fundamental absorption is incident on a solid, electrons are excited into higher empty energy states. After excitation to the conduction band, they may be accelerated by an external electric field to produce electronic conduction $\sigma = n(I,\lambda)e\mu$; where n is the number of charge carriers contributing to conductivity, e is the electronic charge, m is the mobility of the electronic particle in the band, and I and λ are the intensity and the wavelength of the incident light respectively. An increase in electron density in the conduction band is detected as an increase in photocurrent as a function of intensity and wavelength of the incident light or alternatively, conduction can take place by the holes produced in the valence band by the light excitation.

The extremely high resistivity of lead azide required the development of a new spectrometer with an unusually high current measuring sensitivity. An original photoconductivity spectrometer was designed and constructed so as to be capable of measuring currents limited only by the state-of-the-art of present commercial electrometers. Data obtained [8,9,10] for the photoconductivity of lead azide is illustrated in Figure 4. The dark resistivity is on the order of 10^{12} ohm-cm.

The sample preparation and new measuring techniques described here are in no way restricted to lead azide but are more generally applicable. For example, thallous azide has also been prepared by the gas-solid reaction and its optical and photoconductivity properties measured. [11]

One of the critical prerequisites for the measurement of many of the electronic properties is the availability of large, pure single crystals. Small crystals of lead azide have been grown by various techniques with rather limited success. Recently,[12] the technique of cooling ammonium acetate solutions of lead azide has yielded large, pure single crystals up to 1 to 2 centimeters on a side. The crystals are optically clear and of excellent quality.

Techniques have also been devised for orienting, cutting, and polishing the single crystals.

B. Discussion of Results

The structure in the absorption and photoconductivity spectra of lead azide (shown superposed in Figure 5) may reflect a non-uniform density of states in valence band to conduction band transitions or may be due to impurity-to-band transitions or to any of several types of excitons. A minimum in the photocurrent occurs at approximately 375 mμ (millimicron) which is essentially the same wave-length as the first strong optical absorption peak. This minimum is probably due to the onset of a process competing with the production of photocarriers at 375 mμ, which might involve either impurity states or the creation of excitions. The nature or types of excitons which might be associated with this 375 mμ structure is an important feature of the band structure and is therefore discussed in some detail. There is the possibility of intra-anion or intra-cation Frenkel excitons, which are describable in terms of excited states of the azide (N_3^-)

or Pb^{+2} ions, in addition to the localized charge-transfer excitons and Wannier (effective mass) excitons.

Based upon a previous interpretation of alkali azide spectra [13], the first optically observable excited state of the azide ion gives rise to a weak absorption at approximately 230 mμ a transition which creates an excited state of the (N_3^-) intra-anionic exciton. Because of its extreme localization, the transition energy of this exciton is not expected to differ greatly from that observed in the alkali azides; and in fact there is evidence of a weak absorption at 230 mμ in the lead azide thin films.

The excited states of the Pb^{+2} cation correspond to transitions from the ^1S state of the $6s^2$ configuration to the ^3P and ^1P states of the 6s6p configuration. The ^1S and ^3P transitions in the free ion are at 7.49 and 7.98 eV. In solid lead azide, the transition energies will be considerably reduced by crystalline electric fields at the lead sites. Scaling the free ion energies by a factor of 2.2 would place these transitions in lead azide at 3.30 eV (370 mμ) and 3.61 eV (343 mμ). These values correspond fairly well to the major peaks in the absorption spectrum of lead azide. There is evidence in other materials for crystal field shifts of this magnitude. For example, an absorption band has been observed at 3.24 eV in Pb-doped CdI_2 and assigned to internal s-p crystal field transitions of the Pb^{+2} ions. [14] Further, an absorption peak in $PbCl_2$ at 4.5 eV was tentatively assigned to just the kind of Pb^{+2} exciton being discussed here. [15]

The transition energy corresponding to the charge-transfer exciton was determined theoretically by calculating the energy required to remove an electron from an azide ion and place it on a neighboring lead ion. The first step in this determination was to perform detailed calculations of the Madelung potentials [16] as a function of the charge distribution of the azide ion in the complex crystal structure of α-lead azide. [17] The calculations indicate that an ionic model can be applied to lead azide with reasonable success and suggest that the accepted literature value for the lattice energy of lead azide is incorrect. The possibility of structure in the valence band due to the four distinct azide sites in the unit cell was noted. This depends on the azide ion's actual charge distribution which was recently calculated. [18] Using the calculated Madelung potentials in a generalized Von Hippel cycle, the charge-transfer exciton energy for nearest neighbors is estimated to be between 3 and 4 eV in α-lead azide. This value is consistent with a transition at 375 mμ.

Finally, we consider Wannier-type excitons which are describable in terms of perturbed band states in the framework of effective mass theory. The exciton series limits, reduced effective masses, exciton radii, and ionization energies were calculated. The excitons in lead azide appear to be relatively small (at most, 6-9 Å radius). For such small radii, Wannier-like excitons and charge-transfer excitons would be essentially the same. Thus the kinds of exciton which can be responsible for the 375 mμ transition have been reduced to two: intra-cationic excitons and charge-transfer excitons. The results of high pressure measurements currently in progress should distinguish between these. Both interpretations are consistent with a band gap energy of approximately 4 eV.

DIRECT ELECTRONIC INITIATION

A. Theory: General Mechanisms

The development in General Theory predicts that it may be possible to initiate explosives by populating specific electronically excited states. Solid explosives are large band gap semiconductors or insulators. Hence, the lowest and most conveniently accessible intrinsic excited states are the excitons and hole-electron pairs discussed earlier. Because explosives are stable to low levels of stimulation of these kinds of excitations, it is clear that the density of electronic excitation is an important parameter. Thus modes of achieving high densities of electronic excitation qualify as possible mechanisms for direct electronic initiation.[19] Some possible mechanisms will be discussed briefly.

The first mechanism is based on double injection of charge carriers by injecting electrodes which inject excess charge into a sample with the sample becoming in effect a capacitor. The major limitation on injection densities arises from their space charge. But by injecting carriers of opposite charge from two closely-spaced electrodes, the space charges due to the two carriers compensate for each other. Thus suitable electronic injecting contacts may be deposited on crystals, and a voltage applied between the dissimilar electrodes will produce high compensating charge densities by double injection. One electrode is selected for its high work function compared to the work function of the crystal (so that the valence band edge of the solid is bent to the Fermi level) and the other electrode selected for its low work function (so that the conduction band is bent to the Fermi level). Electrons may then be injected from the low work function electrode and hole from the high work function electrode. The inter-electrode distance and applied voltage are then chosen such that injected electrons and holes have adequate lifetimes and mobilities to space charge compensate for each other. The resulting high density of electronic excitation may then initiate fast decomposition and perhaps detonation.

Other mechanisms for direct electronic initiation either involve or are based on negative differential resistivity. This is a phenomenon in which, for certain regions of a material's current-voltage (I-V) characteristic, a <u>decrease</u> in voltage leads to an <u>increase</u> in current. These regions occur in what are called N- and S-shaped I-V characteristics which are depicted in Figures 6 and 7. It can be shown that an S-shaped characteristic can lead to the formation of filamentary channels carrying most of the current. In explosives this corresponds to a localization (and hence large density) of electronic excitation.

A particular example of an I-V characteristic that is basically S-shaped occurs in the Ovshinsky switching phenomenon. [20]

Ovshinsky found that under low applied voltages, ovonic devices conduct current very poorly. As the voltage is raised above a certain threshold, the current rises dramatically, and the high current regime can be maintained at voltages well below theshold. This effect has since been found in a wide variety of materials including organic materials. Most of the materials have two properties in common: low thermal conductivity and the ability to exist in more than one polymorphic form, including an amorphous one. Secondary explosives such as TNT also possess these properties and may thus exhibit the switching phenomenon. The resulting high density of electronic excitation could then lead to initiation.

On the other hand, it is known that the N-shaped I-V characteristic exists in a variety of materials. It may be due to either intrinsic effects (such as those caused by details of the band structure) or extrinsic effects due to defects or dopants. N-shaped characteristics lead to the formation of high electric field regions across thin slices of the crystal perpendicular to a line connecting the electrodes. These regions called high-field domains propagate through the crystal at carrier drift velocites which can be comparable in magnitude to shock velocities. As an example, the current oscillation behavior associated with the Gunn effect [21] is caused by high-field domains which sweep across the crystal. There are theoretical reasons to believe that such mobile excited regions in pseudostable solids could lead to initiation more readily than could static regions of excitation with comparable energy density.

The absorption of optical radiation also excites electronic states as has been noted. These excited states are relatively immobile without the application of electric fields. The combination of light and high electric field, however, can produce excitation transport effects not possible from the light or field alone. Some of these effects could lead to initiation.

B. The Photo-Electronic Initiation Effect

One of the solid state initiation mechanisms has been studied in some detail on lead azide. The most convenient form of lead azide for initiation studies is small diameter pressed pellets since the sample is consumed in each experiment. Initial photoconductivity experiments on pellets indicate a photoresponse qualitatively like that of single crystals and films. However, the quantitative increase in photocurrent over the dark current is small compared to that of crystals, and there is no significant increase in the population of excited electronic states. The apparatus for the initiation experiments is shown in Figure 8. Desired wavelengths were selected by either appropriate filters or by a grating monochromator from a 200 watt Xenon lamp. Threshold electric fields to initiate production-grade lead azide pellets without illumination were 30 kV/cm using silver paint electrodes separated by 1mm. The current-voltage characteristics were found to be ohmic up to the point of initiation, and the typical resistance was 10^{13} ohms (2 orders of magnitude higher than in crystals). Illumination of the area between the electrodes with 400 mμ light (corresponding to the fundamental absorption edge) reduces the threshold voltage for initiation slightly; however, due to the low photoconductivity, the reduction is not spectacular. On a microscopic scale, the pellets are made up of tiny crystallites, and as a consequence the conductivity and electric field distribution is expected to be very inhomogeneous.

For single crystals, threshold electric fields for initiation without illumination were as high as 15 kV/cm. Applying electric fields of 6-7 kV/cm for long periods of time produced no detectable decomposition of lead azide crystals. The current-voltage characteristics displayed a non-ohmic region at fields just below initiation, a phenomenon not found in pressed pellets.

The photocurrent maximum in lead azide crystals is 1000 times more intense than the dark current for relatively low light intensity. Thus the population of excited electronic states is expected to be considerably increased which enhances the conditions for instability. With field strengths below the threshold value, no initiation was observed with low light intensity (10^{15} photons/cm^2/sec) in the red region of the spectrum. However, as the wavelength of the light was decreased at constant light intensity, lead azide crystals were observed to detonate with approximately 400 mμ irradiation. There is some evidence for current oscillations just prior to the initiation; the time between the application of light and the initiation of detonation is generally on the order of a few seconds. The threshold electric field for photoelectronic initiation for 400 mμ irradiation is on the average 1/2 that required with no irradiation. Care was taken to exclude heating effects from stray infrared irradiation, and in fact the photo-electronic initiation effect in lead azide was observed at 77°K. In addition, photo-electronic initiation has been observed in silver azide crystals and most recently in crystals of thallous azide.

Experiments are currently underway to minimize surface effects in the photo-electronic initiation effect. This involves the use of guard rings in a different geometrical configuration than that of Figure 8.

C. Nature of the Photo-Electronic Initiation Effect

The important question of whether the photoelectronic initiation effect is a thermal or non-thermal mechanism may be answered by considering the threshold energy densities required for the initiation of single crystals of explosive azides by intense light flashes. In these materials, for strongly absorbed light pulses of 1-10 microsecond duration, threshold light energy fluxes of 0.1 cal/cm^2 are sufficient to initiate detonation.[22] For flashes lasting near 1 millisecond, threshold energy fluxes are about ten times greater. It has been assumed that the energy from these intense light flashes rapidly degrades to heat and that flash initition is caused by a thermal mechanism. The energy fluxes involved then serve as a useful lower limit for energy densities necessary to initiate detonation thermally in single crystals for energy vs distance profiles similar to the ones in our photo-electronic initiation experiments. To be specific, we assume throughout this discussion that all radiation being considered falls in a spectral region corresponding to an absorption coefficient of 10^5 cm^{-1}, rather strong absorption. Then, as depicted in Figure 9, the bulk of the irradiation is absorbed in a surface layer 1000Å (10^{-5} cm) deep. This gives a threshold absorbed energy density of 10^4 cal/cm^3 for flash-induced initiation or a power density of 10^{10} watts/cm^3 for a 1 μsec flash duration.

In the photo-electronic initiation experiment, two sources of external thermal energy input are present: degradation of absorbed light energy into heat and joule heating due to photocurrents. The light intensity used here corresponds to a power flux of 10^{-1} watts/cm^2 (10^4 watts/cm^3 in the surface layer), a factor 10^6 smaller than the light power density used for flash initiation. In the absence of any heat flow, the present irradiation has to continue for about 1 second to reproduce the energy densities achieved in the flash initiation experiments. But in point of fact, it can be shown that a heat pulse applied uniformly at the surface will diffuse over a surface layer 10,000Å (10^{-4} cm) deep in 1-10 microseconds even for poor thermal conductors. Thus initiation in these azide materials is not expected for such low light intensities applied without an electric field, regardless of duration of the irradiation. This expectation is indeed borne out experimentally: decomposition can occur at these intensities but not the initiation of detonation.

The second source of thermal energy mentioned was joule heating due to photoconductivity. Because the photoconductivity is so much stronger than the dark conductivity, it is clear that almost all the photocurrent flows in the thin 1000Å layer at the surface where the absorption is strong (Figure 9). Estimating the power absorption density in different regions of the surface layer depends on the electric field distribution and on whether the current flows over the entire surface area or in a thin filament connecting the electrodes. For a uniform field distribution, the joule heating power density for currents measured just below threshold is 10 watts/cm^3, 1000 times less than that due to the light irradiation alone. It is not possible to exceed the power density input of the light by considering that most of the voltage drop takes place over a small fraction of the interelectrode distance because the resulting fields would be in the dielectric breakdown range (about 10^6 V/cm). Although dielectric breakdown cannot be discounted as an initiation mechanism, it is not a strictly thermal mechanism. Further, even under the most extreme assumptions, thermal initiation requires all the photocurrent to be carried by a filament less than 1000Å (10^{-5} cm) in diameter with local fields approaching the dielectric breakdown limit. The formation of filaments of this nature could not be explained by simple thermal arguments. Their possible role has been discussed above.

Thus we see that the thermal energy densities achieved in our photo-electronic initiation effect are far too small to explain the effect by simple thermal arguments. It would appear that detonation is instead initiated by an electronically excited state of the crystal (which is itself a result of the combination of electric field and light) as the general theoretical argument in General Theory predicts.

DISCUSSION

The apparently non-thermal nature of the photo-electronic initiation effect, its dependence on the wavelength of optical irradiation, and its non-ohmic I-V characteristic below the initiation threshold electric field all suggest a direct electronic mechanism. The details of that mechanism are not yet fully understood and must await the more complete experimental characterization of the effect currently underway in this Laboratory. It could involve any of the general mechanisms described above in Fundamental Electronic Properties: injection, ovonic-like switching, high-field domains, or more sophisticated effects involving electric-field induced motion of dense electronic excitation. The non-ohmic I-V characteristic tends to support either injection or high-field domains assisted in some manner by light absorption (particularly because of the evidence for current oscillations immediately preceding initiation).

The possibility of achieving the direct electronic initiation of secondary explosives is, as mentioned earlier, a particularly exciting prospect. The discussion of metastable electronic states in General Theory applies to secondary explosives as well as to primaries. Secondary explosives are mostly organic compounds, and the specific mechanisms for direct electronic initiation in these compounds could well be quite different from those in azide compounds. The experimental program on secondaries initially concentrated on the preparation of amorphous thin films (to search for ovonic-like switching) and on achieving space-charge compensated double injection. Our current preliminary work includes the growth of high-quality crystals and the characterization of their optical and conductivity properties.

In general, secondary explosives are much less sensitive to impact initiation than are primary explosives such as lead azide. Although there is presently no fundamental correlation between sensitivities to different stimuli, the relative sensitivities of a group of explosives to the same stimulus, for example mechanical impact, is useful for ordering their relative stabilities. Table I shows the Picatinny Arsenal impact sensitivities for lead azide, thallous azide, and the secondary explosives PETN and HMX. In this test, thallous azide and PETN have comparable sensitivities and fall between lead azide and HMX in relative sensitivity. They are both a good deal less sensitive to impact than lead azide but rather more so than is HMX (or most other secondary explosives). The important point is that we have already achieved direct electronic initiation in an explosive solid (thallous azide) that is comparable in impact sensitivity to a secondary explosive, PETN.

CONCLUSIONS

The results demonstrate that by applying a closely coordinated theoretical and experimental effort in which all of the necessary solid state techniques are employed, the electronic energy level structure of solids as complex as the metal azides and other explosives can be elucidated.

A new technique has been developed for the preparation of thin films of inorganic, explosive solids which is capable of producing films of excellent optical quality. Low temperature (4°K) high resolution spectrophotometers have been designed and assembled for the determination of the optical properties of explosives and pseudostable materials, and the optical absorption of lead, thallous, and other metal azides have been determined.

A sensitive, high resolution, variable temperature, photoconductivity spectrometer has been designed and assembled which is capable of measuring photoconductivity and other transport properties of explosives and related solids. These properties have been determined for the heavy metal azides for the first time. Madelung and simple band structure calculations have been performed on lead azide. The calculations, coupled with the optical and transport property measurements, led to the first consistent description of the electronic band structure of lead azide or of an explosive solid.

Several new mechanims have been proposed for the direct initiation of primary and secondary explosives. All of these are being explored theoretically and experimentally.

Direct non-thermal initiation of lead azide has been discovered by a photo-electronic mechanism. This is the first observation of a non-thermal mechanism for the initiation of an explosive and clearly deomonstrates the relationship between the electronic energy band structure and the explosive properties of solids and has obvious application to new concepts in fuze technology.

Photo-electronic initation has been observed in the less sensitive explosive thallous azide. This has helped establish the rationale for proceeding and generalizing this type of investigation to include organic secondary explosives.

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TABLE I

Impact Sensitivity of Selected Explosives Using Picatinny Arsenal Drop Test (23)

Sample	Lead Azide	Thallous Azide	PETN	HMX
Drop Height [(a)] (in.):	4-6	9-10	9	14

(a) Drop Height at which a 2kgm weight [illegible] 0% of samples.

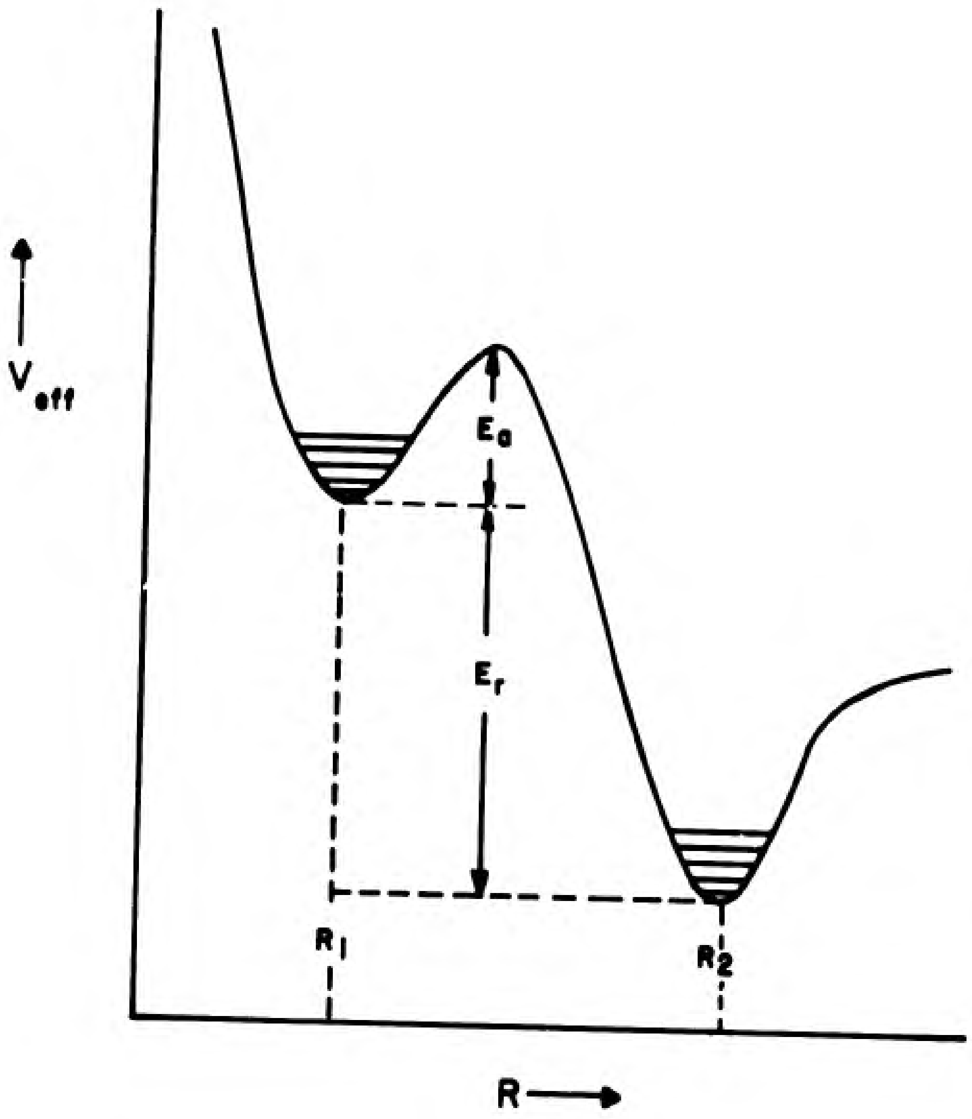

FIGURE 1 - Reaction Coordinate Diagram Depicting the Metastable Character of Reactive Solids

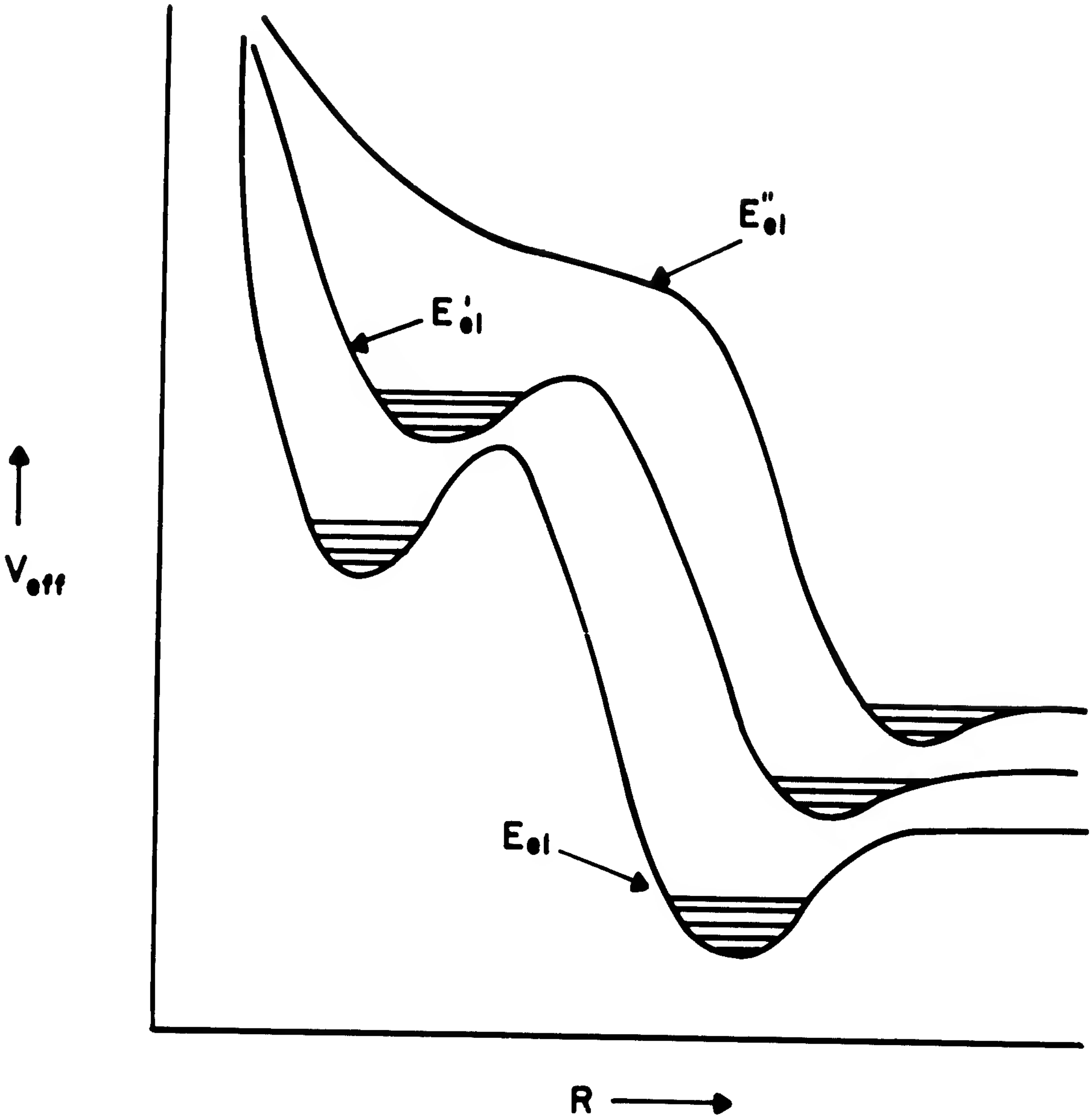

FIGURE 2 - Reaction Coordinate Diagram Depicting Possible Changes in Activation Energy Due to Excited Electronic States

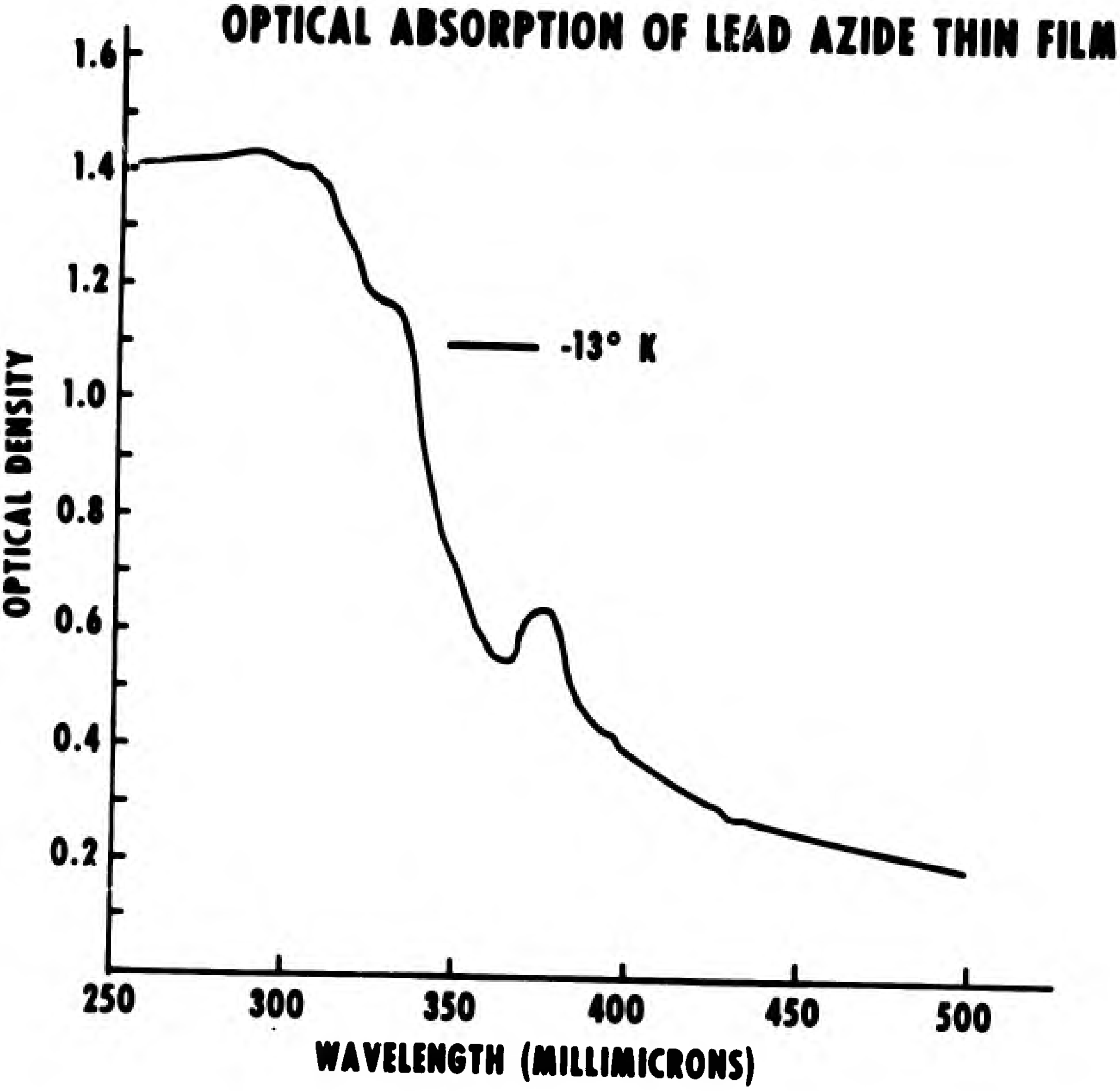

FIGURE 3 - Optical Absorption Spectrum of a Lead Azide Thin Film

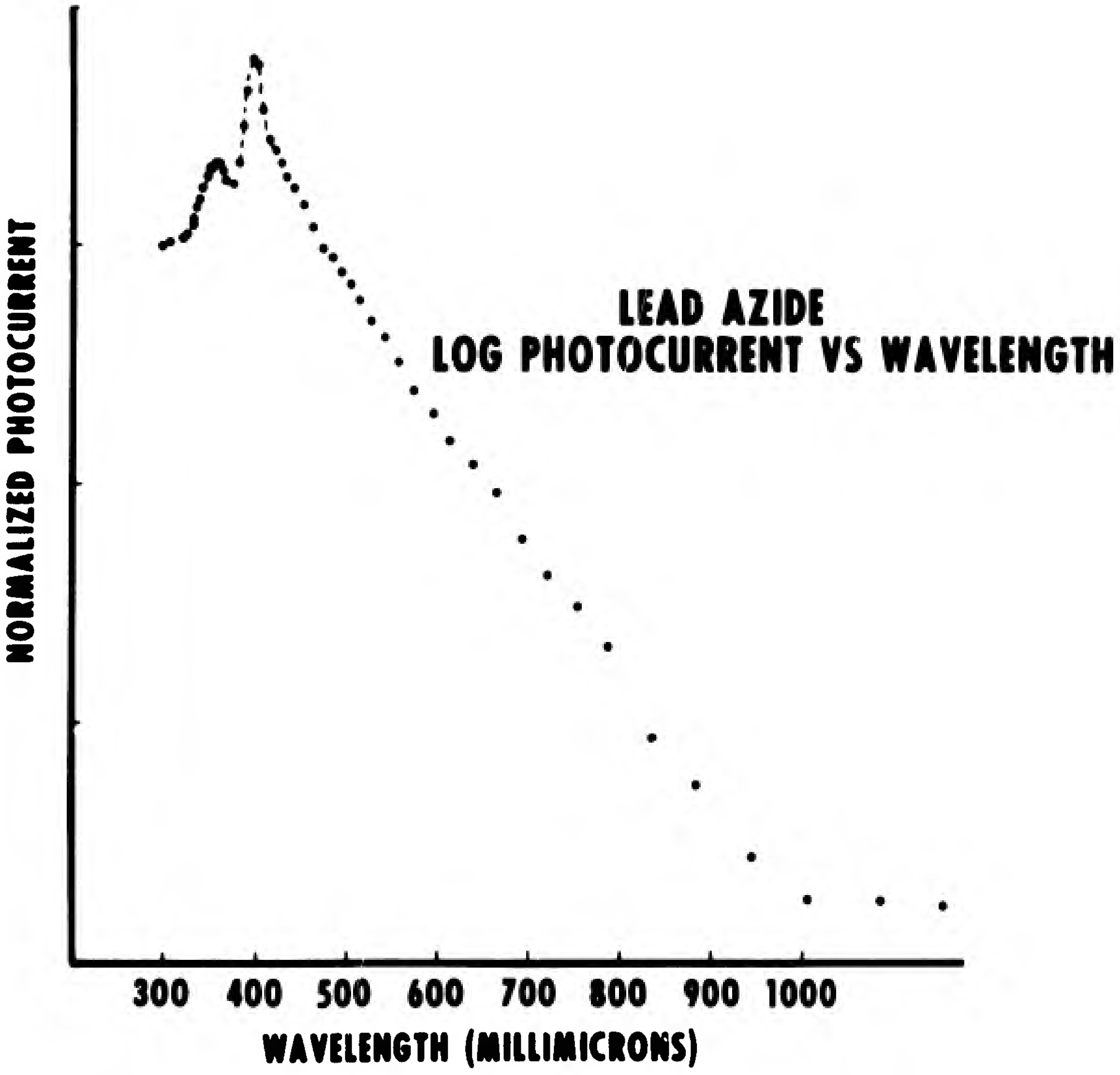

FIGURE 4 - Spectral Response of Photocurrent of Lead Azide

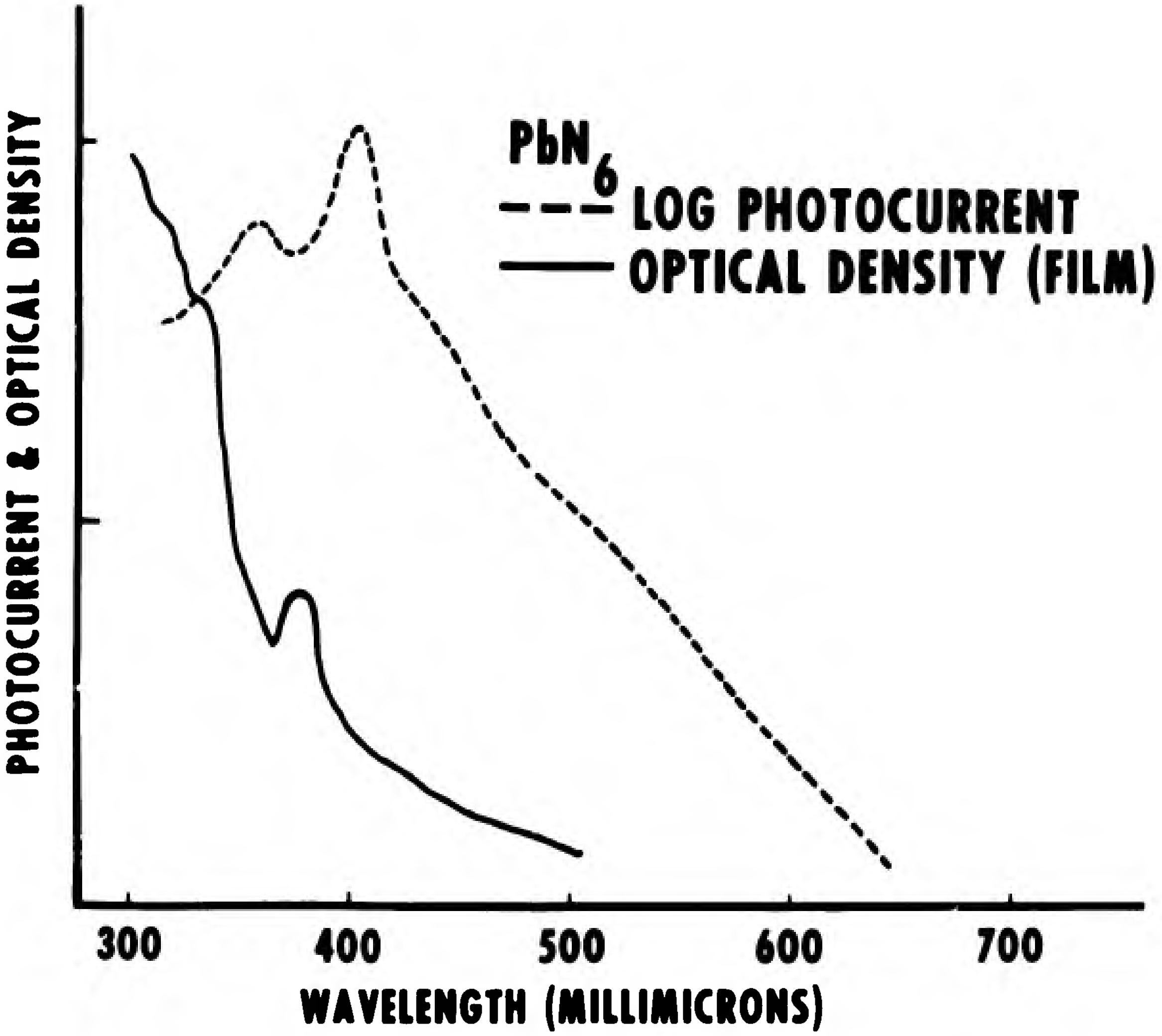

FIGURE 5 - Spectral Response of Optical Absorption (—) and Photo-Current (---) in Lead Azide

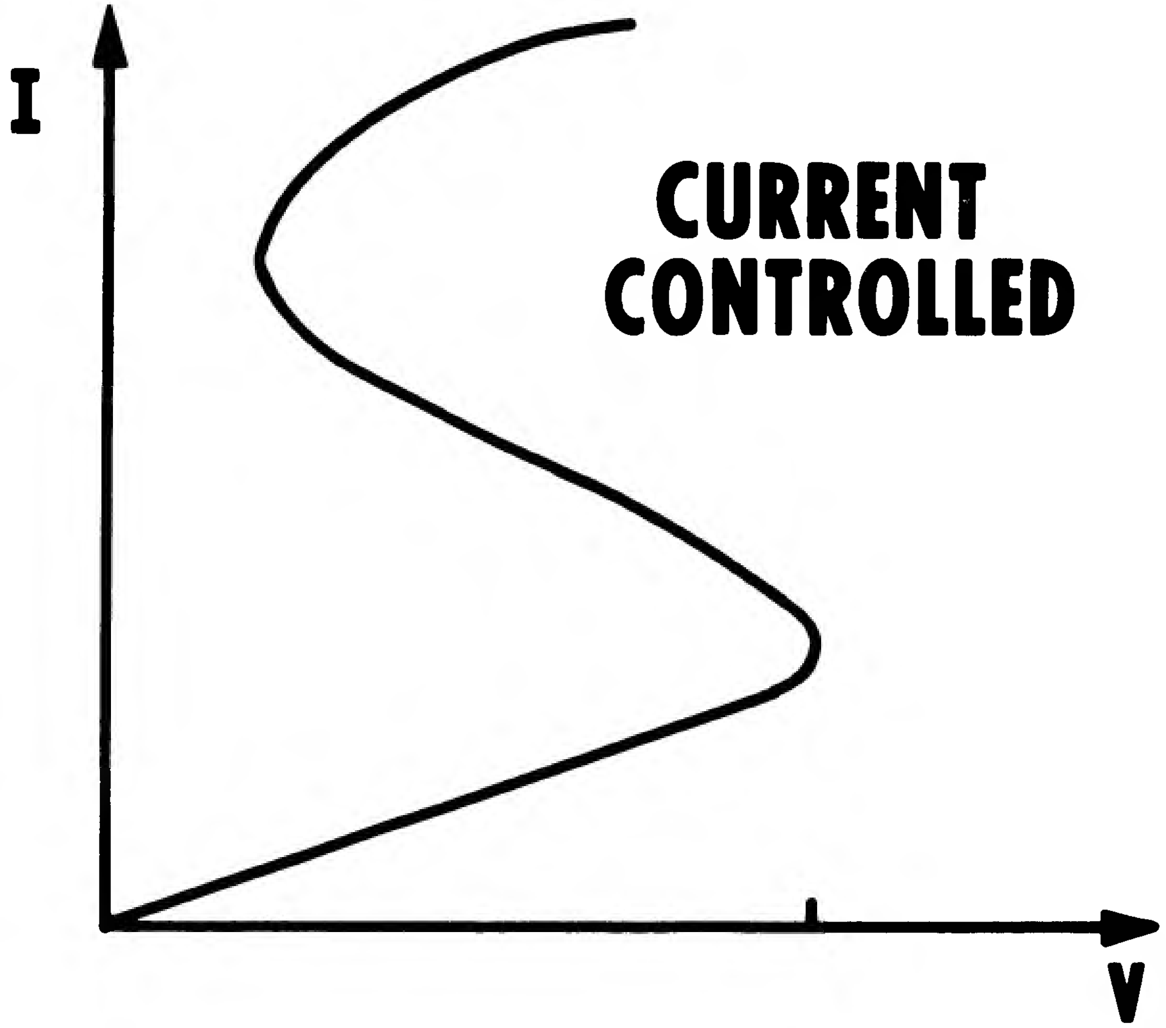

FIGURE 6 - S-shaped Current-Voltage Characteristic Showing Current Controlled Differential Negative Resistance

VOLTAGE CONTROLLED

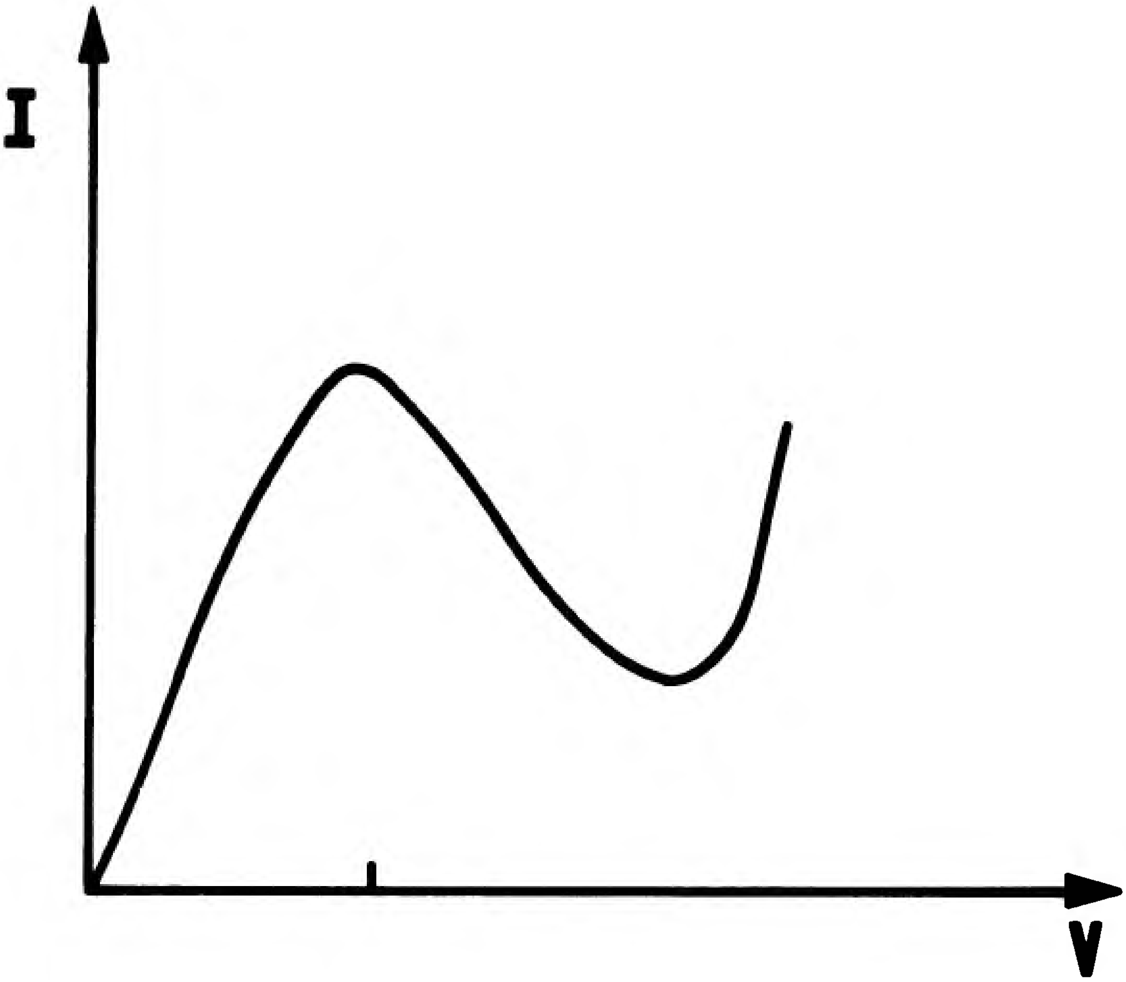

FIGURE 7 - N-shaped Current-Voltage Characteristic Showing Voltage Controlled Differential Negative Resistance

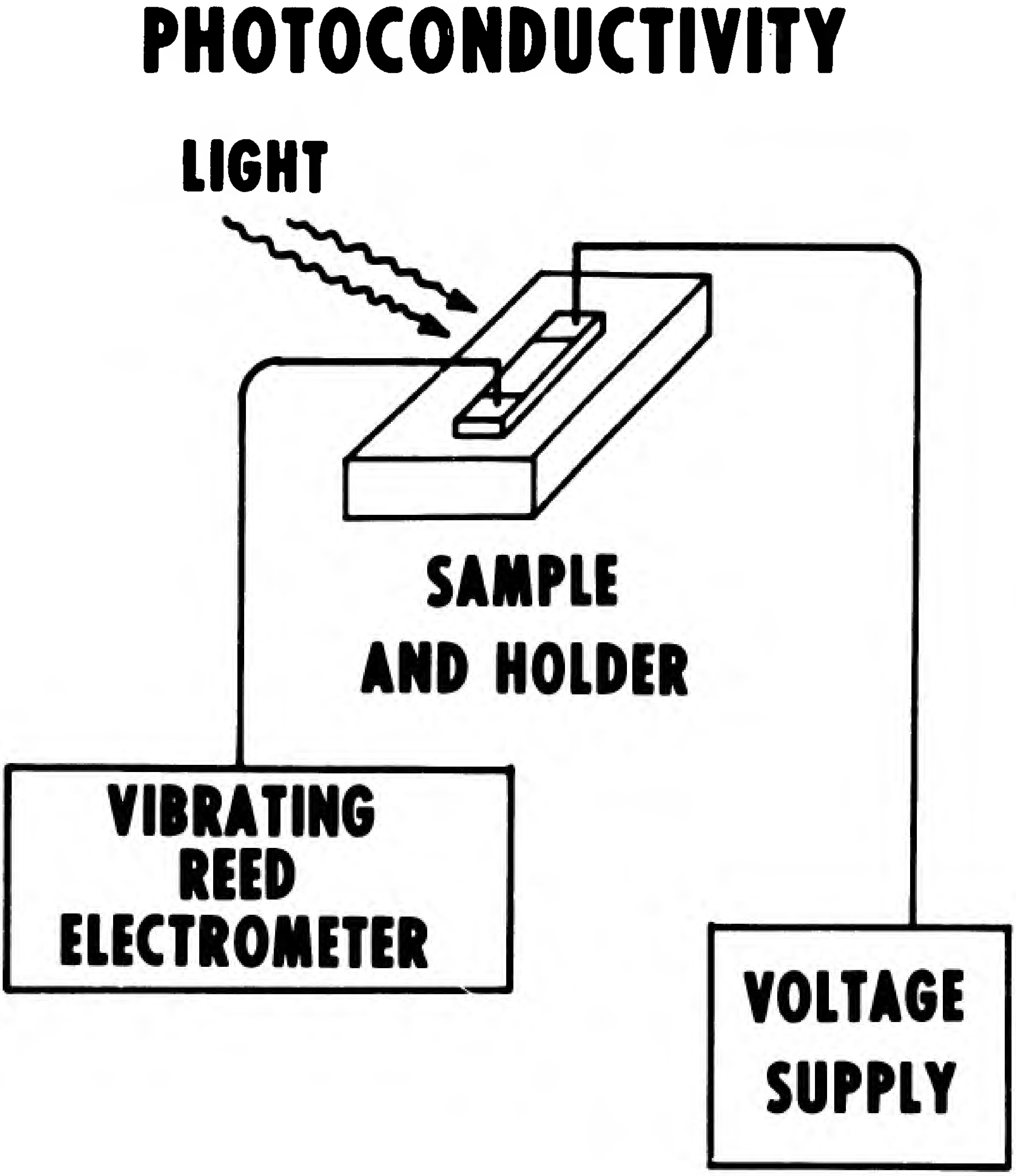

FIGURE 8 - Experimental Arrangement for Investigation of the Photo-Electronic Initiation Effect

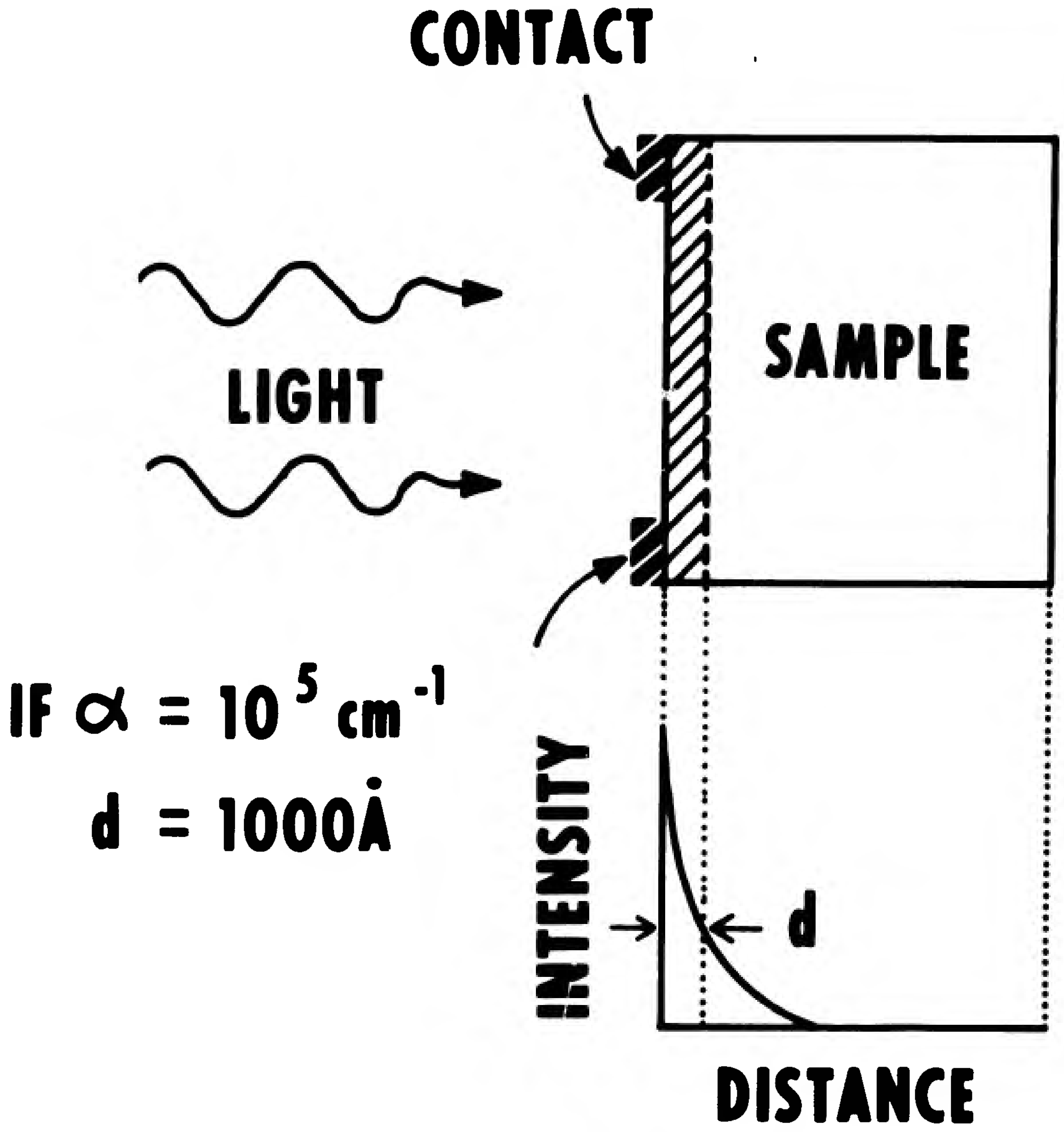

FIGURE 9 - Effective Volume of Photo-Electronic Excitation for Direct Initiation